



# Article Phase Transformations and Tellurium Recovery from Technical Copper Telluride by Oxidative-Distillate Roasting at 0.67 kPa

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**Abstract:** This paper presents the results of a study of phase transformations occurring in coppertelluride by-products during its processing of oxidation-distillate roasting at low pressure. The results show that copper telluride is oxidized through intermediate compounds to the most stable tellurate (Cu<sub>3</sub>TeO<sub>6</sub>) at low temperatures. The increase in the roasting temperature above 900 °C and the presence of an oxidizer favor the copper orthotellurate decomposition. Thus, the tellurium extraction rate is 90–93% at a temperature of 1000 °C, the oxidant flow rate is  $2.2 \times 10^{-2} \text{ m}^3/\text{m}^2 \cdot \text{s}$ , and the roasting time is 60–90 min. One of the decomposition products is copper oxide alloy, which is the basis of the residue. The second product is tellurium in oxide form, which evaporates and then condenses in the cold zone of the condenser in crystalline form. The main constituent phase of the condensate is tellurium oxide (TeO<sub>2</sub>), which can be further processed during one operation to elemental chalcogen by thermal reduction or electrolytic method.

Keywords: recovery; tellurium; copper telluride; distillation; roasting; phase composition; oxide

# 1. Introduction

The main raw material source of tellurium is slime from electrolysis production of copper, a multicomponent material that contains copper from 1 to 50, silver up to 29, gold up to 2.18, selenium from 2 to 15, and tellurium up to 22 wt%. As a rule, copper in slime is represented in elemental form, and selenium and tellurium in the form of copper and noble metal chalcogenides. The variety of chemical and phase compositions of slimes determines quite a wide range of methods for their processing. Some developed methods are described in [1–5].

To date, both hydrometallurgical and pyrometallurgical methods have been used to recover tellurium from copper electrolyte sludge [6–8].

A schematic diagram of classical tellurium production during the processing of copper electrolyte slime [6,7,9] is shown in Figure 1. Full implementation of the process enables selective recovery of target commercial metals from slime: gold, silver, selenium, tellurium, as well as copper.

As can be seen, the slime undergoes leaching in the first stage. The insoluble residue containing gold and silver is sent to the noble metals' workshop. Tellurium concentrates in a solution that is first directed to the precipitation of selenium and silver, then to the precipitation of tellurium itself. The solution obtained at this stage is returned to copper production, and the precipitate is used for the production of elemental tellurium. Vacuum distillation and/or zone melting are used to obtain high-purity tellurium (up to 6 N) at the final stage of the process flow. The combined use of these two pyrometallurgical methods enables the obtaining of tellurium with semiconductor purity. It should be noted that, in the case of low-quality extraction of selenium at the beginning of the process, an azeotropic Te-Se mixture will form during the distillation of tellurium [10,11], which will adversely affect the quality of elemental tellurium.



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**Copyright:** © 2022 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). Frequently, the cementation of metallic copper is used for tellurium precipitation from the solution. As a result, insoluble copper telluride containing phases of both stoichiometric (Cu<sub>2</sub>Te) and nonstoichiometric compositions (Cu<sub>2-x</sub>Te) are formed. Copper telluride, in addition to tellurium with varying purity, is a valuable product of tellurium production [12–15]. Some plants prefer to accumulate or sell copper telluride at relatively low prices rather than to further separate tellurium and copper. This approach is associated with technological and technical difficulties due to the amount of stages, the significant consumption of reagents, the generation of large amounts of wastewater containing heavy metals, etc.

Therefore, the development of a cost-effective and environmentally friendly process for the recovery of Te and Cu from technical copper telluride is of great importance to the metallurgical industry.

Information in the field on the developments of telluride recovery from copper telluride is practically absent in the literature. We found only two works by Chinese scientists [15,16] that proposed to improve the preparatory stage of metallic tellurium electrolysis.

Traditionally, the middling is first dissolved by oxidative alkaline leaching with the addition of NaOH [7,9]. Then, the tellurium-containing solution is sent for electrolysis, while the copper-containing residue is for copper recovery.

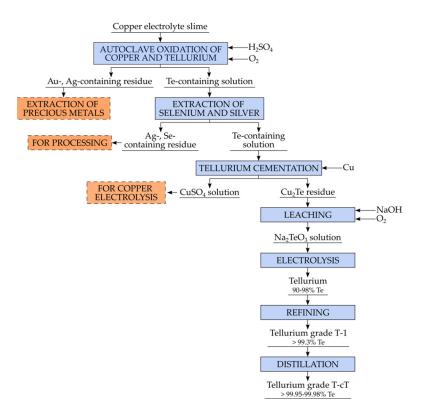


Figure 1. Copper electrolyte slime processing diagram.

The authors studied the possibility of oxidative leaching of copper telluride with the addition of NaOH at both an increased and atmospheric pressure in one of their works [15]. Oxygen was used as an oxidizing agent. The best results were achieved with autoclave leaching; more than 95% of tellurium was transferred into the solution in the form of Na<sub>2</sub>TeO<sub>3</sub>. The precipitate exclusively contained crystalline phase Cu<sub>2</sub>O that enabled it to be returned to copper production. The technology developed for tellurium deposition in the form of TeO<sub>2</sub> involved the neutralization of a tellurium-containing solution with sulfuric acid. Then, the obtained tellurium dioxide, containing up to 97% TeO<sub>2</sub>, could be sent to the electrolytic workshop for metallic tellurium separation.

The second method [16] suggested the use of  $H_2O_2$  as an oxidizer. The process also consisted of two stages: oxidative-alkaline leaching and precipitation of tellurium from the solution in the form of its oxide. The tellurium recovery rate after the alkaline leaching stage that was performed in two stages was 93%. The overall recovery of tellurium was almost 90%; the TeO<sub>2</sub> content in the resulting residue was 96%. The authors also proposed sending the tellurium-containing residue for electrolytic production of elemental tellurium.

As can be seen from the above data, the developed methods do not help to reduce the number of traditional drawbacks that accompany hydrometallurgical processes. Pyrometallurgical methods are well-combined with the schemes intended to obtain the pure element and are the most preferred. However, they have not found application in practice or research development in this area because of the high temperatures in the process. An effective way to reduce the process temperature by 100–200 °C is to conduct the process at reduced pressure. In addition, the use of a vacuum also contributes to the improvement of working conditions for the personnel as a consequence of the fact that the process is performed in a hermetic and compact apparatus.

Obtaining tellurium by Cu<sub>2</sub>Te decomposition in actual conditions by the vacuumthermal method is not possible due to a small dissociation pressure of liquid copper telluride: 0.7 kPa at 1780 °C. However, the saturated vapor pressure of TeO<sub>2</sub> is about 0.02 kPa and is already at 733 °C. Therefore, this study was performed to develop a method for the recovery of tellurium in the form of an oxide with the use of the pyrometallurgical method at low pressure with its further processing to elemental tellurium without any technological and technical difficulties. In particular, phase transformations were defined, and the influence of temperature and process duration on tellurium recovery at oxidativedistillation roasting of commercial copper telluride was determined.

## 2. Materials and Methods

#### 2.1. Methodology

The laboratory installation (Figure 2) consisted of a horizontal tubular electric furnace RT 50/250/13 (Nabertherm, Germany), where the reactor used for this study was placed. The reactor was a quartz tube that had channels at the ends for air supply and gas phase evacuation. A 2HVR-5DM UHL4 vacuum pump (Vacuummash, Kazan, Russia) was used to create a vacuum in the system. The pressure in the reactor was controlled by a barometer-aneroid and a McLeod monometer. The oxidizer flow rate was controlled by a PC-3A rotameter (Teplopribor, Moscow, Russia).

The experimental procedure was as follows: A copper telluride sample (weight, 3 g) was loaded into an alundum boat. Then, the boat was placed in a split (lengthwise) alundum condenser. The condenser, in turn, was placed in a quartz reactor. The ready reactor was placed in a furnace that was heated to the required temperature so that the copper telluride sample was in the isothermal zone. A vacuum system and an oxidizer feeding system were connected to the reactor. The beginning of the experiment was considered the moment when the pressure and flow rate of the oxidant reached the specified values. The systems of gas supply and evacuation were disconnected at the end of the experiment. The reactor was removed from the furnace and cooled in the air. The obtained copper alloy and tellurium condensate were weighed and analyzed.

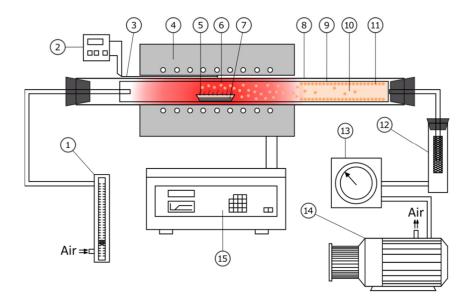
The process temperature varied in the range from 500 to 1000  $^{\circ}$ C, and the exposure time was from 5 to 90 min.

Pressure in the system was maintained at 0.67 kPa. The mentioned pressure is necessary for transferring a tellurium oxide into a gas phase in the decomposition of copper orthotellurate ( $Cu_3TeO_6$ ), which formed during the oxidation of copper telluride.

Air oxygen was used as an oxidizer. The airflow rate was chosen to be constant and maximal at  $2.2 \times 10^{-2} \text{ m}^3/\text{m}^2 \cdot \text{s}$ , considering the capacity of the evacuating vacuum system that provided the reactor pressure of 0.67 kPa.

The material composition was studied by X-ray fluorescence analysis using a wave dispersive combined spectrometer, Axios PANalytical (Malvern Panalytical Ltd., Malvern, UK).

An X-ray diffractometer D8 Advance Bruker and Cu-K $\alpha$  radiation and the ICDDPDF-2 reference database (2020) were used to identify the phase composition.



**Figure 2.** Horizontal vacuum unit with a split condenser: (1) rotameter, (2) temperature controller in the reaction zone, (3) control thermocouple, (4) electric furnace, (5) boat, (6) isothermal zone, (7) sample, (8) reactor, (9) split condenser, (10) condensation zone, (11) condensate, (12) filter, (13) barometer-aneroid, (14) vacuum pump, and (15) furnace controller.

#### 2.3. Materials

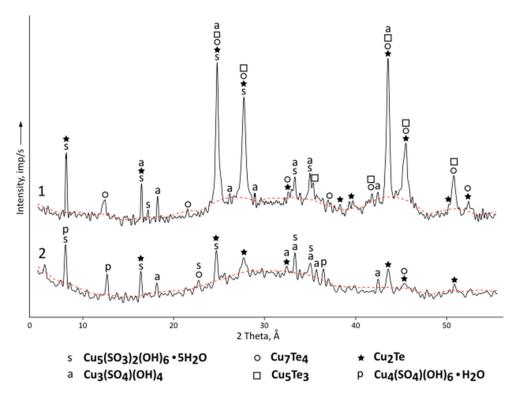
The tellurium-containing middling ( $Cu_2Te$ ) used in our study was obtained from copper electrolyte slime at the refinery of Kazakhmys Smelting LLP (Balkhash, the Republic of Kazakhstan).

Copper telluride (Figure 3), in its appearance, was a pelletized, wet-black material and odorless at the time of delivery. There were inclusions of malachite color on the surface of agglomerates. The moisture content was 29%.

A large proportion of amorphous halo (78.3%) due to the scattering from disordered phases was established under the X-ray phase-analysis results. The crystalline part of the middling amounted to 21.7% and mainly consisted of copper telluride phases of stoichiometric (Cu<sub>2</sub>Te, PDF 00-057-0477) and no-stoichiometric (Cu<sub>7</sub>Te<sub>4</sub>, PDF 02-1222 Cu<sub>5</sub>Te<sub>3</sub>, PDF 00-057-0196) compositions. In addition to copper tellurides, crystalline phases of oxidative reaction products of the copper were found in the material (Cu<sub>5</sub>(SO<sub>3</sub>)<sub>2</sub>(OH)<sub>6</sub>·5H<sub>2</sub>O—PDF 51-0321, Cu<sub>3</sub>(SO<sub>4</sub>)(OH)<sub>4</sub>—PDF 07-0408). Apparently, the mentioned hydroxosulfates are the main phase of malachite-colored phenocrysts on the surface of copper telluride [14]. The probable cause of material oxidation is insufficient washing of copper telluride from CuSO<sub>4</sub> solution after tellurium cementation operation on copper from tellurous acid.

Differences in composition and structure were determined when comparing the appearance and phase composition of the two samples of the copper telluride [14,17], which were acquired at different times but analyzed at the same time. Apparently, oxidative processes proceed over time in the material under the influence of its humidity, the presence of sulfate ions, and storage conditions. As a result, the mentioned differences were observed.

The sample of copper telluride was further analyzed before the experiments intended to study the phase transformations occurring in the material during oxidative-distillate roasting. It was found from the analysis results that the copper telluride structure was quite strongly amorphized. Both copper hydroxosulfates and copper tellurides of variable composition were found among the crystalline phases. The humidity of the middling was 9%.



**Figure 3.** X-ray diffraction patterns of a tellurium-containing middling of Kazakhmys Corporation LLC: (1) at the time of delivery and (2) before studies.

The material composition of copper telluride samples is shown in Table 1: sample 1 at the time of delivery and sample 2 before the study. More detailed information on the physicochemical properties of the product we studied can be found in [13,17].

Tab.	le 1.	Compositio	on of tell	lurium-con	taining	middling.
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Sample					E	lements, w	vt%				
Sample	0	Al	Si	S	Cl	Fe	Cu	As	Se	Te	Pb
1	18.88	0.11	0.03	2.09	0.29	0.02	47.19	0.11	0.04	31.22	0.02
2	29.46	0.01	0.02	2.01	0.23	0.02	41.50	0.10	0.02	26.63	-

For this study, a representative sample of copper telluride (sample 2) was crushed to a fineness of less than 0.315 mm.

## 3. Results and Discussion

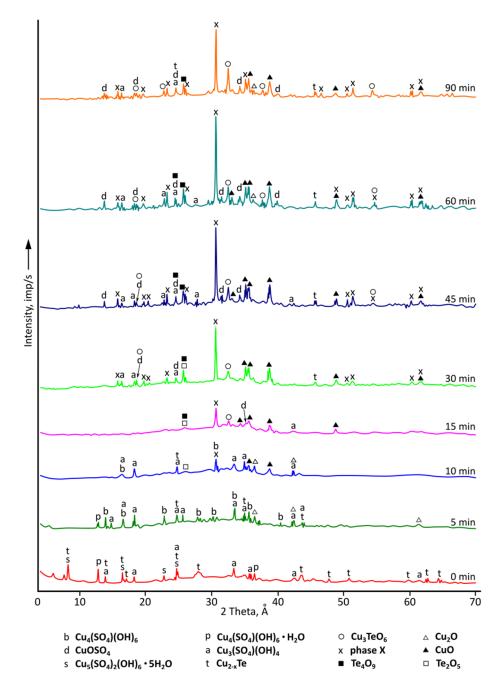
3.1. Low-Temperature Roasting (500 and 700 °C)

It is known that the volatility of tellurium dioxide is low up to its melting temperature (733 °C) and is the only stable tellurium oxide at temperatures above 430 °C [18]. The value of TeO<sub>2</sub>-saturated vapor pressure at its melting temperature of 733 °C is 0.026 kPa according to [19], and about 0.019 kPa according to [6]. Therefore, it is obvious that the distillation process at temperatures below 900 °C is inexpedient.

However, the phase transitions occurring at low temperatures are more expressed than at high temperatures. It should be expected, based on the literature sources, that strandbergite  $(Cu_5(SO_4)_2(OH)_6 \cdot 5H_2O)$  and posnjakite  $(Cu_4(SO_4)(OH)_6 \cdot H_2O)$  will eventu-

ally transform into the brochantite form  $(Cu_4(SO_4)(OH)_6)$  (at a low content of  $SO_2/SO_4^{2-})$ ) or in the form of anthlerite  $(Cu_3(SO_4)(OH)_4)$  (at a high content of  $SO_2/SO_4^{2-}$ ), depending on the  $SO_2/SO_4^{2-}$  content in the reaction space [20]. The formation of copper oxides and elemental tellurium is the first assumed of the oxidative reactions at low temperatures. Then, it will be oxidized to  $TeO_2$ , which will further react with copper oxides to form  $CuTe_2O_5$ and/or  $CuTeO_3$  if enough tellurium accumulates [21]. The formed copper tellurites are also expected to be oxidized to orthotellurate ( $Cu_3TeO_6$ ) [18].

The results of qualitative (Figure 4) and semiquantitative (Table 2) analyses of the phase composition of the cinders obtained at 500  $^{\circ}$ C were as follows.



**Figure 4.** X-ray patterns of residues were obtained at 500  $^{\circ}$ C, 0.67 kPa, and different roasting durations.

Phase	Phases Content (%) at the Roasting Time, min								
T Hase	5	10	15	30	45	60	90		
			at 500 $^{\circ}\mathrm{C}$						
$Cu_3(SO_4)(OH)_4$	27.0	24.6	9.0	6.6	5.3	5.2	5.1		
$Cu_4(SO_4)(OH)_6$	27.0	13.0	-	-	-	-	-		
$Cu_4(SO_4)(OH)_6 \cdot H_2O$	10.9	-	-	-	-	-	-		
CuOSO <sub>4</sub>	_	-	8.4	7.8	10.5	12.0	13.5		
Cu <sub>2-x</sub> Te	18.5	13.9	8.0	5.1	4.6	6.0	8.1		
Cu <sub>3</sub> TeO <sub>6</sub>	_	-	10.0	15.4	20.6	27.0	31.5		
CuO	_	19.4	43.0	41.7	34.7	31.3	22.4		
Cu <sub>2</sub> O	12.2	20.0	-	-	-	_	5.1		
Te <sub>2</sub> O <sub>5</sub>	4.4	9.1	8.0	5.2	5.3	_	-		
Te <sub>4</sub> O <sub>9</sub>	-	-	14.0	18.2	18.9	18.0	14.2		
			at 700 °C						
Cu <sub>3</sub> (SO <sub>4</sub> )(OH) <sub>4</sub>	5.5	_	_	_	_	_	-		
CuOSO <sub>4</sub>	8.3	5.0	-	-	-	-	-		
Cu <sub>3</sub> TeO <sub>6</sub>	43.8	47.1	71.3	80.0	94.1	95.5	94.5		
CuTeO <sub>3</sub>	6.8	7.1	5.2	-	-	-	-		
CuTeO <sub>4</sub>	2.9	13.2	9.6	8.5	-	-	-		
$Te_3Cu_2O_7$	9.1	-	6.0	-	-	-	-		
CuO	11.5	12.8	7.9	11.5	5.9	4.5	5.5		
Te <sub>4</sub> O <sub>9</sub>	12.1	14.8	-	_	_	_	-		

**Table 2.** Phase composition (wt%) of low-temperature roasting residues (for Figures 4 and 5 (hereinafter, the quantitative analysis is given without considering the unknown phase, X.)).

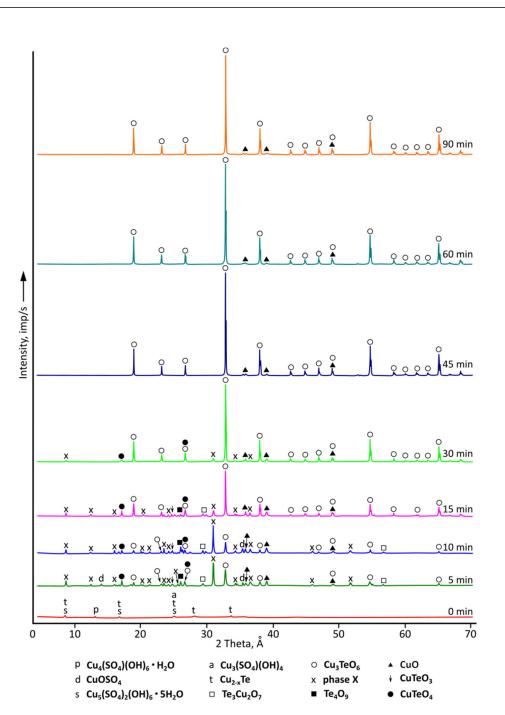
The decomposition of  $Cu_5(SO_4)_2(OH)_6 \cdot 5H_2O$  and  $Cu_4(SO_4)(OH)_6 \cdot H_2O$  occurs quite intensively and is accompanied by the joint formation of anthlerite and brochantite. Apparently, anthlerite is initially formed. The concentration of  $SO_2/SO_4^{2-}$  decreases with the removal of sulfate ions by the oxidant flow, resulting in the formation of brochantite.  $Cu_4(SO_4)(OH)_6$  and anthlerite further decompose to form dolerophanite (CuOSO<sub>4</sub>), copper (I) oxide, and water. At the same time, brochantite exists for a short time, while the anthlerite decomposition process is prolonged and did not end in the studied time interval.

The formation of copper and tellurium oxides was noted during the copper telluride oxidation at the initial stages, which agrees quite well with the data [21]. However, tellurite phases of copper (CuTeO<sub>3</sub> and CuTe<sub>2</sub>O<sub>5</sub>), elemental tellurium, and tellurium dioxide phases at 500 °C were not detected. This may have been due to the disordered structure of the material, as evidenced by the presence of an amorphous halo on the diffractograms of the samples.

For the oxide forms of tellurium, the presence of intermediate phases  $Te_2O_5$  and  $Te_4O_9$  were established that decompose into dioxide and free oxygen at 500–520 °C according to [22], and according to [23] at 595 °C (at atmospheric pressure). In addition, during the roasting process, the possible formation of telluric anhydride  $TeO_3$  dissociates to  $Te_2O_5$  and  $Te_4O_9$  when it is heated above 400 °C [19,24].

In our study, the crystalline products of the interaction between copper and tellurium oxides were intermediate phase X (d = 2.91340 Å, at  $2\theta$  = 30.66 Å) and copper orthotellurate (d = 2.748606 Å,  $2\theta$  = 32.55038 Å). The latter may have been a product of the interaction of both copper tellurites, with copper (I) oxide in the air atmosphere and the "initial" CuO and TeO<sub>3</sub> [25]. The nature of the X phase should be studied further.

A similar mechanism of hydroxosulfates destruction and the oxidation of copper telluride was shown by the results of the study performed at 700  $^{\circ}$ C (Figure 5, Table 2).



**Figure 5.** X-ray patterns of residues were obtained at 700 °C, 0.67 kPa, and different roasting durations.

The complete decomposition of copper hydroxosulfates within the first 15 min of roasting and the intensive formation of phase X and copper orthotellurate through intermediate compounds were established. Phases of metatellurite CuTeO<sub>4</sub>, tellurite CuTeO<sub>3</sub>, and tellurite copper Te<sub>3</sub>Cu<sub>2</sub>O<sub>7</sub> were found in addition to these compounds in the residues. Despite the existence of congruent melting tellurates Te<sub>3</sub>Cu<sub>2</sub>O<sub>7</sub> and TeCu<sub>2</sub>O<sub>3</sub> in the Cu<sub>2</sub>O-TeO<sub>2</sub> system [26], the formation of the Te<sub>3</sub>Cu<sub>2</sub>O<sub>7</sub> compound in the air was questioned in [27]. According to the authors, the Te<sub>3</sub>Cu<sub>2</sub>O<sub>7</sub> is most probably represented mainly by CuTe<sub>2</sub>O<sub>5</sub> pyrotellurite molecules. In this case, the formation of tellurites and orthotellurate involves only tenorite, which is an oxidation product of cuprite. Sufficiently complete oxidation of the material to copper orthotellurate occured at roasting times of 45 min or more. The Cu<sub>3</sub>TeO<sub>6</sub> phase content in the cinders was 93.1–95.5 wt%.

# 3.2. High-Temperature Roasting (900 and 1000 °C)

The copper orthotellurate  $Cu_3TeO_6$  formed in the process of oxidative-distillate roasting is stable up to temperatures of 810–880 °C according to the literature data [25,28,29].

The results of X-ray phase analysis of cinders from high-temperature roasting showed (Figures 6 and 7, and Table 3) that the total decomposition of copper hydroxosulfates occurred at an exposure time of 10 min. Additionally, in the case of low-temperature roasting, the formation of Cu<sub>3</sub>TeO<sub>6</sub> was accompanied by a decrease in the amount of phase X. Copper orthotellurate did not completely decompose at 900 °C for the 90 min of exposure. At 1000 °C, 10 min of roasting was sufficient for the total decomposition of Cu<sub>3</sub>TeO<sub>6</sub>; cinders from longer roasting durations were represented by a mixture of copper oxides.

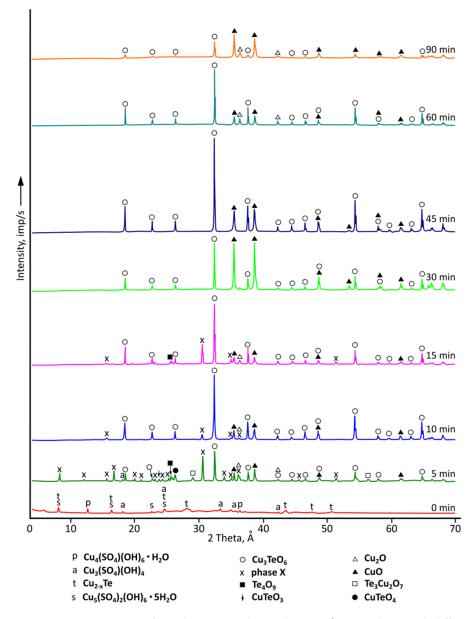
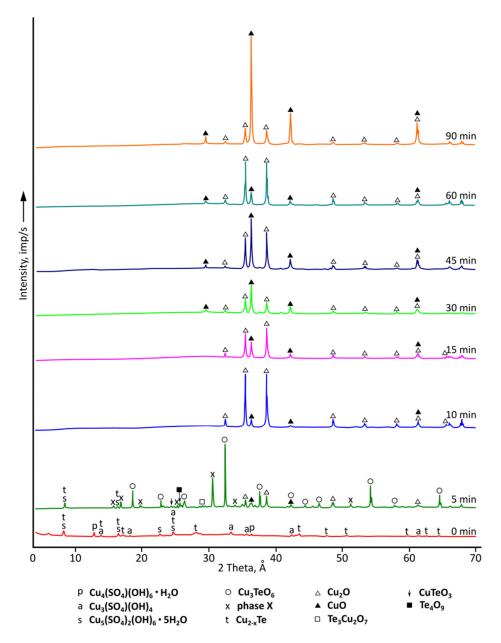


Figure 6. X-ray patterns of residues were obtained at 900  $^\circ$ C, 0.67 kPa, and different roasting durations.



**Figure 7.** X-ray patterns of residues were obtained at 1000  $^{\circ}$ C, 0.67 kPa, and different roasting durations.

There are very scarce literature data regarding the issue of the decomposition products of copper orthotellurate. Thus, it is indicated in [30] only that it breaks down to  $CuTeO_4$  and copper oxide CuO. Additionally, in [28], the following mechanism was established in the study of the thermal behavior of copper metatellurite in the air:

- Metatellurite is destroyed by the reaction at 540–630 and 700–725 °C: 3CuTeO<sub>4</sub>  $\rightarrow$  Cu<sub>3</sub>TeO<sub>6</sub> + 2TeO<sub>2</sub> + O<sub>2</sub>;
- − Then, at 840–880 °C, the interaction of copper orthotellurate and tellurium oxide occurs, resulting in the formation of copper tellurite with the emission of oxygen in the gas phase:  $Cu_3TeO_6 + 2TeO_2 \rightarrow 3CuTeO_3 + 1/2O_2$ .

The results of our studies showed that the decomposition of Cu<sub>3</sub>TeO<sub>6</sub> in the air flow proceeded by the req: Cu<sub>3</sub>TeO<sub>6</sub>  $\rightarrow$  3CuO + TeO<sub>2</sub> + 1/2O<sub>2</sub>.

This difference from the literature data is due to the fact that the saturated vapor pressure of TeO<sub>2</sub> reaches a value of about 1.33 kPa at a process temperature of 900  $^{\circ}$ C,

according to [19], and at approximately 0.53 kPa, according to [6]. Therefore, there will be an accumulation of formed oxide in the solid product at atmospheric pressure [28]. In our study (where the system pressure was 0.67 kPa), the tellurium oxide was transferred into the gas phase and removed from the reaction zone by an oxidant flow. Such conditions contributed to the decomposition of orthotellurate rather than its transition into the copper tellurite form.

61.	Phases Content (%) at the Roasting Time, min								
Sample	5	10	15	30	45	60	90		
			at 900 °C						
$Cu_3(SO_4)(OH)_4$	4.3	_	_	_	_	_	-		
Cu <sub>3</sub> TeO <sub>6</sub>	27.2	59.1	5.1	47.7	77.2	55.4	30.3		
CuTeO <sub>3</sub>	6.5	_	_	_	_	_	-		
CuTeO <sub>4</sub>	19.3	_	-	_	_	_	-		
Te <sub>3</sub> Cu <sub>2</sub> O <sub>7</sub>	11.5	_	-	_	_	_	-		
CuO	23.6	32.3	22.9	49.7	22.8	32.8	55.3		
Cu <sub>2</sub> O	4.1	8.6	14.3	2.6	_	11.8	14.3		
Te <sub>4</sub> O <sub>9</sub>	3.5	-	4.7	-	-	-	-		
			at 1000 °C						
Cu <sub>3</sub> TeO <sub>6</sub>	56.6	-	-	-	-	_	-		
CuTeO <sub>3</sub>	2.9	_	-	_	_	-	-		
Te <sub>3</sub> Cu <sub>2</sub> O <sub>7</sub>	4.3	_	_	_	_	_	-		
CuO	14.4	81.7	76.2	27.6	35.4	87.1	15.5		
Cu <sub>2</sub> O	6.3	12.0	20.3	60.9	56.1	12.9	82.7		
Te <sub>4</sub> O <sub>9</sub>	4.5	_	_	_	_	_	-		

Table 3. Phase composition (wt%) of high-temperature roasting residues (for Figures 6 and 7).

#### 3.3. Influence of Roasting Temperature and Time on Tellurium Recovery at 0.67 kPa

The dependence of the tellurium extraction rate and speed on the roasting time at different process temperatures is shown in Figure 8. The extraction rate (%) was taken as the ratio of the amount of evaporated tellurium to its initial mass, and the amount of tellurium evaporated per unit time from per unit geometric area of evaporation (boats) was taken as the extraction speed ( $g/cm^2 \cdot s$ ).

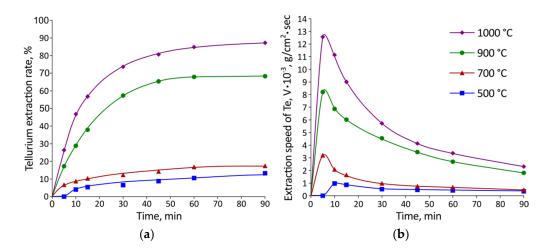


Figure 8. Dependence of the rate (a) and speed (b) of tellurium extraction on the duration of exposure at different temperatures.

It can be seen from the given data that, at 500 and 700 °C, the degree of tellurium extraction was insignificant and did not exceed 20% during an hour and a half exposure.

An increase in the oxidative-distillate temperature of up to 900–1000 °C had a positive effect on tellurium recovery that reached about 70% at 900 °C and about 90% at 1000 °C during an hour and a half of roasting. A sharp rise in the step curve during high-temperature roasting was observed within the first 15 min; then, its growth slowed down. At the same time, the speed curve tended to grow within the first 5 min. An increase in the process duration over 60 min at 700–1000 °C had little effect on the tellurium recovery from commercial copper telluride. It should be noted that an acceptable value (93–98%) of the recovery rate is reached at a process temperature of 1100 °C [31].

The obtained condensate is a dense crystalline powder of white color (Figure 9), well-separated from the condenser surface. The presence of crystalline phases of tellurium dioxide TeO<sub>2</sub> (PDF 00-042-1365) in an amount of 67.7% and tellurium oxysulfate Te<sub>2</sub>O<sub>3</sub>(SO<sub>4</sub>) (PDF 01-070-0135) at 32.3% was established in the condensate by diffractometric analysis (Figure 10). The presence of tellurium oxysulfate can be explained by a violation of the technological process for washing technical copper telluride from sulfuric acid solution in the hydrometallurgical production scheme.



Figure 9. Condensate from the copper telluride roasting on the surface of the condenser (**a**) and in the free state (**b**).

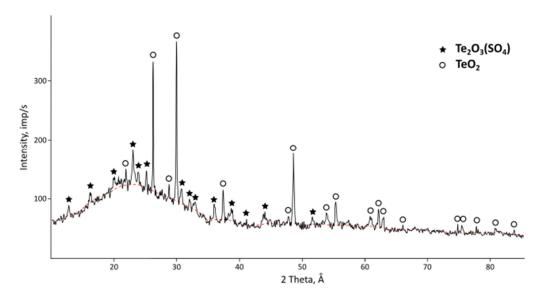


Figure 10. X-ray pattern of obtained condensate.

The condensate is the initial middling intended to obtain elemental tellurium by known technologies.

# 4. Conclusions

We found as a result of this work that copper telluride is oxidized to the most stable tellurate Cu<sub>3</sub>TeO<sub>6</sub> through intermediate compounds in the process of oxidation roasting at low temperatures. Thus, one of the intermediate compounds is the unidentified phase, X. The increase in the roasting temperature above 900 °C at a pressure of 0.67 kPa and in an oxidant flow process contributed to the copper orthotellurate decomposition. Thus, the value of the tellurium extraction rate is 90–93% at 1000 °C (pressure—0.67 kPa, the oxidant flow speed is  $2.2 \times 10^{-2} \text{ m}^3/\text{m}^2 \cdot \text{s}$ , and roasting time is 60–90 min). One of the decomposition products is copper oxide alloy, which is the basis of the residue. The second product is the oxide forms of tellurium that evaporate and then condense in crystalline form in the cold zone of the condenser.

The condensate is a dense, fine crystalline powder of white color that separates well from the surface of the condenser. The process of condensate collapsing from the condenser walls in a loose form can be arranged with an appropriate technical design.

The main constituent phase of the condensate is tellurium oxide, which can be processed into elemental chalcogen in one operation by thermal reduction or electrolytic method.

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